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Electronic spectrum of phenyl isocyanate

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Analysis of the vibrational structure of the electronic absorption spectrum of phenyl isocyanate has been carried out. The analysis indicates that the molecule has a nonplaner structure belonging to C_s point group. The f-value of the electronic transition and the spectroscopic moment of the NCO group are computed. It is concluded that on substitution of NCO group produces a large migration moment.

1. INTRODUCTION

Some features of fluorescence spectrum of phenyl isocyonate were described by Rabalais *et al* (1969a, 1969b) and its vibrational spectra were analysed by Ham and Willis (1960) and Stephenson *et al* (1961). Katritzky *et al* (1970) discussed the possible orientation of the NCO group in this molecule. It was felt that for a proper understanding of the nature of the electronic transition, a detailed vibronic analysis of the electronic absorption spectrum and computation of f-value of transition and spectroscopic moment of the substituent NCO group might be helpful. In this paper, the observed characteristics of the electronic spectrum of the molecule are discussed.

2. EXPERIMENTAL

A Carl Zeiss D$_2$E deuteron lamp was used for providing ultraviolet continuum. Other experimental details were the same as described earlier (Mallick & Banerjee, 1974).

3. RESULTS AND DISCUSSION

The ring vibrations of phenyl isocyanate molecule were assigned on the basis of C_{2v} symmetry by Stephenson *et al* (1961) who, however, hinted that the actual symmetry could be C_s. For C_{2v} symmetry, the electronic transition giving rise to the band system should be $B_2 \leftarrow A_1$ and the expected features of the transition are well known. It is seen that the spectrum exhibits a strong 0,0 band (table 1). If the symmetry be C_{2v}, then some of the excited state funlamentals would belong to a_1 species.

Table 1. Absorption bands of phenyl isocynate vapour

Wave number (cm^{-1}) and Intensity.	Difference from the 0 — 0 band.	Assignment.
36117 (w)	236	0 — 236
36208 (m)	145	0 — 145
36287 (s)	66	0 — 236 + 173
36353 (s)	0	0 — 0
36526 (m)	173	0 + 173
36713 (ms)	360	0 + 360
36813 (ms)	460	0 + 460
36917 (s)	564	0 + 564
37109 (s)	756	0 + 756
37330 (s)	977	0 + 977
37498 (s)	1145	0 + 1145
37653 (ms)	1300	0 + 1300
37839 (ms)	1486	0 + 2 × 756 0 + 1486
37954 (ms)	1601	0 + 460 + 1145
38056 (ms)	1703	0 + 756 + 977
38288 (s)	1935	0 + 2 × 977
38406 (s)	2053	0 + 2 × 460 + 1145 0 + 564 + 2 × 756
38584 (ms)	2231	0 + 3 × 756
38703 (ms)	2350	0 + 460 + 756 + 1145
38793 (ms)	2440	0 + 2 × 756 + 977

An observed 1-1 transition (table 1) involving a b_2 vibration of frequency 236 cm^{-1} in the ground state and 173 cm^{-1} in the excited state would also be consistent with a $B_2 \leftarrow A_1$ transition in a C_{2v} molecule. But two b_1 vibrations, one having frequency 145 cm^{-1} in the ground state and the other of frequency 460 cm^{-1} in the excited state are also coupled with the transition in the contravention of the selection rules for $B_2 \leftarrow A_1$ transition. In view of this, it seems that assumption of C_{2v} symmetry is not quite justified and for a more reasonable interpretation of the vibronic spectrum, the symmetry of the molecule should be taken as C_s.

In this connection, it is to be noted that Kartritzky *et al* (1970) had suggested that the phenyl isocyanate molecule is not planar. The NCO group is inclined to the benzene ring and lies in the plane perpendicular to the benzene ring passing through C_1-C_4 axis. The plane of symmetry is thus perpendicular to the plane of the phenyl ring and containing the C_1-C_4 axis. The electronic transition $B_{2u} \leftarrow A_{1g}$ becomes for this molecule $A'' \leftarrow A'$. As the analysis shows (table 1 & 2), one of the most active vibrational modes has frequency 756 cm^{-1} and this represents, on the basis of vibrational

Table 2. Active ground and excited state vibrational frequencies (in cm^{-1}) of phenyl isocyanate

Ground State Vibrational Spectra.	Ultraviolet Spectra.	Excited State Ultraviolet Spectra.	Assignment For C_{2v} point group	Assignment For C_s point group*
245	236	173	b_2	a″
145	145	—	b_1	a′
385 or 395	—	360	a_1 or a_2	a′ or a″
496	—	460	b_1	a′
616	—	564	b_2	a″
761	—	756	a_1	a′
1003	—	977	a_1	a′
1170	—	1145	a_1	a′
1334	—	1300	b_2	a″
1512	—	1486	a_1	a′

(*The plane of symmetry is perpendicular to phenylring and contains the C_1—C_4 axis).

assignment of Stephenson *et al*, the *ring breathing* vibration. Another prominent excited frequency 977 cm^{-1} may be related to the b_{1u} mode 12 of benzene (Stephenson *et al*, 1961) which involves C-C-C angle deformation. These skeletal vibrations are in the plane of the ring. They are of a′ symmetry and may effectively take part in vibronic perturbation in a π-electronic transition. The ring deformation vibrations having frequency 145 cm^{-1} perpenlicular to the plane of the molecule in the excited state is also of a′ symmetry for this molecule as also the vibration yielding the excited state frequency 460 cm^{-1}.

Therefore all these vibrations should appear prominently in the allowed A″←A′ electronic transition. The remaining fundamental 236 cm $^{-1}$ belong to a″ class and may appear weakly in the trasition while a 1-1 transition involving this mode in the ground and excited state may be expected in the spectrum. The vibrational structure of the electronic spectrum of the molecule is, therefore, in accord with the proposed non-planar structure of the phenyl isocyanate molecule.

Table 3. The f-values and the spectroscopic moment

Benzene		Phenyl isocyanate		
f	I_0	f	I	m
(1.6×10^{-3}) *a*				
(2.4×10^{-3}) *b*	162	1.5×10^{-2}	1000	(−) 29 *d*

a Sponer and Teller (1941).
b This work.
c Using Platt's expression (Platt, 1951).
d (−) sign is taken since NCO is an electron- withdrawing group.

The f- value of transition of phenyl isocyanate, measured in cyclohexane solution is 1.5×10^{-2} and following Platt (1951), the spectroscopic moment m for NCO substitution has been calculated to be (−) 29 (table 3), the minus sign indicating that the substituent group is meta-directing or electron-withdrawing. The f-value and the shift of the 0-0 band of phenyl isocyanate with respect to that of benzene are of comparable magnitudes with those due to phenol (Robertson & Matsen, 1950 a,b). The spectroscopic moment is also comparable to the moment (+) 34 computed for phenol by Platt (1951). These observations show that substitution of NCO group produces a large migration moment. Similar remark was also made by Rabalais *et al.* Incidentally, it may be noted that in proposing the nonplaner structure for phenyl isocyanate, Katritzky *et al* (1970) pointed out that for this molecule there is a preference for overlap between the π-ring system and the sp^2-hybridized long pair orbital on nitrogen.

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